CHEMISTRY LETTERS, pp. 507-508, 1975. Published by the Chemical Society of Japan

THE HIGH SELECTIVITY OF MgO AND CaO FOR THE FORMATION OF 2-CARENE FROM 3-CARENE

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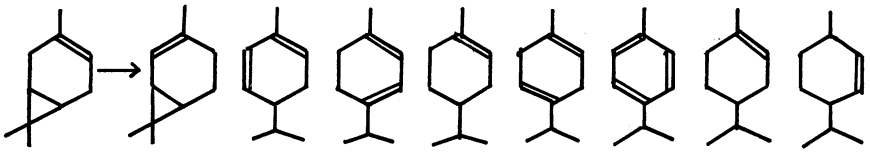
The selectivity of various oxide catalysts for the isomerization of 3-carene were studied at 50-200°C. 2-Carene was predominantly formed over MgO, CaO, SrO, Y_2O_3, La_2O_3, and ZrO_2, while p-cymene and various menthadienes over Ce_2O_3, TiO_2, Al_2O_3, and SiO_2-Al_2O_3. BaO, ZnO, and ThO_2 produced only p-cymene, but their activities were very low.

The isomerization of 3-carene to 2-carene was reported to take place over Na or K metal on Al_2O_3, potassium tert-butoxide-dimethyl sulfoxide, and the complexes of alkali metals with organic compounds such as γ-picoline, ethylene diamine, o-chlorotoluene etc.1) However, no work has been done on the selective isomerization catalyzed by metal oxides. Since the alkaline earth metal oxides were found to be active and selective catalysts for the double bond isomerizations of 1-butene to 2-butene2) and of α-pinene to β-pinene,3) we have examined the catalytic action of the oxides together with the other oxides for the double bond isomerization of 3-carene.

MgO, CaO, SrO, and BaO were obtained by calcining $Mg(OH)_2$ (Kanto Chem. Co.), $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$ (Merck Co.), $CaCO_3$ (Merck Co.), $Ca(OH)_2$ (Kanto Chem. Co.), $SrCO_3$ (Merck Co.), and BaO (Merck Co.) at the temperatures indicated in Table 1 for 2 hr in a helium stream. ZnO, Y_2O_3, La_2O_3, Ce_2O_3, and ThO_2 were prepared by the hydrolyses of their nitrates with ammonia water, followed by washing, drying and calcining as above. TiO_2 and ZrO_2 were prepared similarly from titanium tetrachloride and zirconium oxychloride, respectively. ZnO, ThO_2, TiO_2, and ZrO_2 were calcined in air at 500°C for 5 hr before calcining in a helium stream. Active Al_2O_3 (Nishio Industries Co., Ltd.) and SiO_2-Al_2O_3 (Nikki Chemical Co., Al_2O_3 content; 15 wt. %) were calcined at 500°C for 2 hr in a helium stream. The reaction was carried out at 50-200°C by a pulse method4) and the reaction products were analyzed by gas chromatography with a 5.5 m column of polyethylene glycol 20M on celite 545.

The reaction products of 3-carene (I) were 2-carene (II), p-mentha-1,5-diene or α-phellandrene (III), α-terpinene or p-mentha-1,3-diene (IV), limonene or p-mentha-1,8-diene (V), γ-terpinene or p-mentha-1,4-diene (VI), p-cymene (VII), terpinolene or p-mentha-1,4(8)-diene (VIII), mentha-2,4(8)-diene (IX) and unidentified products.



I II III IV V VI VII VIII IX

As shown in Table 1, 2-carene was predominantly formed over MgO, CaO prepared from $CaCO_3$, SrO, Y_2O_3, La_2O_3 and ZrO_2. In particular, MgO and CaO prepared from $CaCO_3$ showed more than 90 % selectivity for the formation of 2-carene (II). It is surprising that CaO prepared from $Ca(OH)_2$ gave 70 % of p-cymene, the activity being two times higher than that prepared from $CaCO_3$. On the other hand, various menthadiene (III, IV, V, VI, VIII, IX) and p-cymene (VII) were formed over Al_2O_3, Ce_2O_3, TiO_2, and SiO_2-Al_2O_3. Al_2O_3 and TiO_2 produced comparatively large amount of an unidentified product having a retention time longer than IX, while the other catalysts formed two unidentified products having retention times shorter than II (supposedly isolimonene included). BaO, ZnO, and ThO_2 produced only p-cymene, but their activity was very low.

Since MgO,[3] CaO,[3] SrO,[5] Y_2O_3,[6] La_2O_3,[6] and ZrO_2[7] are known to have basic property on the surfaces, the preferential formation of 2-carene found over the catalysts is considered to be due to the action of the basic sites. The preferential formation of p-cymene over CaO prepared from $Ca(OH)_2$ is difficult to explain and will be the subject of further research.

Table 1. Isomerization of 3-carene

Catalysts	Temp. of calcination °C	Reaction temp. °C	Contact time mg ml^{-1}min	Conversion %	Selectivity (%)								
					II	III	IV	V	VI	VII	VIII	IX	Others
$MgO^{a)}$	500	100	1.66	43.8	93.0					3.2			3.8
$MgO^{b)}$	500	100	3.36	46.1	95.2					2.8			2.0
$CaO^{c)}$	900	100	1.71	36.8	96.0	1.6							2.4
$CaO^{b)}$	600	100	1.68	73.8	28.8					70.0			1.2
$SrO^{c)}$	900	100	1.68	42.5	66.6					30.0			3.4
BaO	900	150	1.71	1.6						(100.0)			
ZnO	500	200	1.66	1.3						(100.0)			
Al_2O_3	500	100	1.68	74.2	5.1		15.9	21.1	6.9	3.7	17.4		29.9
Y_2O_3	700	100	1.69	53.7	72.8					25.9			1.3
La_2O_3	700	100	1.69	51.1	84.3					11.7			4.0
Ce_2O_3	700	200	1.70	9.4	50.6	11.8				33.9			3.7
ThO_2	500	150	1.65	1.8						(100.0)			
TiO_2	500	100	1.67	31.3	34.5	10.2		26.6	2.0	3.6		11.5	11.6
ZrO_2	500	100	1.68	43.0	86.5					11.4			2.1
SiO_2-Al_2O_3	500	50	0.113	58.0	13.5		11.1	7.5	3.3	33.9	3.5		27.2

a) prepared from $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$, b) from the hydroxides, c) from the carbonates

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(Received April 2, 1975)